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Ultrafine FeSe Nanoparticles Embedded into 3D Carbon Nanofiber Aerogels with FeSe/Carbon Interface for Efficient and Long-life Sodium Storage

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Abstract: The key challenge for high-performance sodium-ion batteries (SIBs) is the exploitation of appropriate electrode materials with a long cycling stability and high rate capability. This study reports the synthesis of a composite of ultrafine FeSe NPs and carbon nanofiber aerogel (CNFA) as anode material for SIBs. The composite features ultra-small (~ 5 nm) NPs of FeSe uniformly embedded in interconnect three dimensional (3D) carbon nanofiber with large surface area, highly conductive network, and robust structural stability. As expected, the FeSe-CNFA-700 sample delivers a capacity as high as ~ 313 mA h g⁻¹ at 2000 mA g⁻¹ after 1000 cycles and ultrahigh rate capability up to 20000 mA g⁻¹. The significantly improved electrochemical performance could be attributed to the unique structure that combines a variety of advantages: easy access of electrolyte to the 3D network structure, pseudocapacitive charge storage and fast Na ion diffusion processes. The results confirm the intercalation of Na⁺ into the 3D ultrafine FeSe nanoparticles/carbon nanofiber aerogel is enhanced through the strong interaction between FeSe nanocrystals and the carbon layer. The DFT calculations demonstrates that the unique FeSe/carbon layer interface in 3D network structure can enhance Na storage due to the small energy barrier and negative adsorption energy.

1. Introduction

As promising candidate replacements for ubiquitous lithium-ion batteries (LIBs), sodium-ion batteries (SIBs) have attracted great attention due to the abundance and low cost of sodium resource [1-3]. However, typical graphite anode materials for LIBs, shows poor electrochemical performance in SIBs. Only a limited number of Na^+ ions can be intercalated into graphite (about NaC_{70}) and the resultant theoretical capacity is as low as 31 mA h g^{-1} . However, Na^+ has a larger radius than Li^+ , which directly affects the mass transport and storage in the electrochemical process.[4, 5]. So many attempts have been made to develop carbonaceous anode materials to enhance the Na^+ storage with a reversible capacity of approximately $250\text{-}300 \text{ mA h g}^{-1}$, such as amorphous carbon, hard carbon, and N-doped carbon nanosheets [6-9]. However, concerning the limitation of carbon structures, further capacity increase cannot be expected due to limitation of Na^+ host sites. Therefore, it is great challenge to find high-capacity anode materials for SIBs to meet the requirement of high densities.

Recently, numerous SIBs anode materials with high capacities have been developed, including Sn-based, P, Ge, metal selenides, metal oxides, and metal sulfides [10-13]. Among them, transition metal selenides (TMSe), such as NiSe_2 nanoplates, urchin-Like CoSe_2 , FeSe_2 microspheres and MoSe_2 nanoplates, have attracted much attention due to their easily-controlled morphology and high theoretical specific capacity [14-16]. As a typical layered compound, FeSe ($a = b = 3.73 \text{ \AA}$, and $c = 5.77 \text{ \AA}$, space group P4m2) possesses a simple crystal structure. Theoretically, Na^+ ions could be easily intercalated between the FeSe_4 -tetrahedra layers. According to first-principles calculations within density functional theory (DFT), Na^+ ions have a diffusion barrier in FeSe_4 -tetrahedra layers as low as 0.46 eV . However, there are few reports on FeSe

anode materials for SIBs [17]. Maybe this is ascribed to three reasons. Firstly, compared with other TMSe_s such as NiSe₂, CoSe₂, FeSe₂, more serious volume change (~ 235 %) of FeSe often cause serious electrochemical agglomeration and pulverization during Na⁺ insertion/extraction process, resulting in a poor capacity and bad cycling performance [18, 19]. Secondly, the high rate behavior of Na⁺ storage with bulk FeSe is seriously restricted by its sluggish ion diffusion kinetics [19]. Recent works have shown that interfacial Na storage may occur when viable solid–liquid or solid–solid interfaces are designed in the battery system by constructing either porous structure or mixed phase composition. Finally, FeSe is a poor electrical conductor as a semiconductor material as well as other TMSe, resulting in fast capacity attenuation. Only all the issues can be addressed, the layered FeSe can become promising candidate anode materials for SIBs.

In this paper, we report the synthesis of ultrafine FeSe nanoparticles (NPs, ~ 5 nm) embedded in 3D net-like carbon nanofiber aerogel (noted as FeSe-CNFA) via a sustainable seaweed-template strategy. Sodium alginate (SA), a seaweed extract product, can form “egg box” structure after ion-exchange with Fe³⁺ due to coordination with four α -L-guluronate blocks of alginate, which is the key for the synthesis [20-27]. On one hand, the “egg box” coordination process is along with gelation of an aqueous SA solution, which easily makes the formation of highly porous 3D carbon aerogel after dehydration via a freeze-drying and subsequent selenylation at high temperatures. On the other hand, the nanoconfinement effect of Fe³⁺ ions by “egg box” can efficiently control the homogeneous and narrow size distribution of the FeSe NPs in the aerogel support. When evaluated as an anode material for SIBs, FeSe-CNFA exhibits a capacity as high as 313 mA h g⁻¹ at 2000 mA g⁻¹ after 1000 cycles. It also displays a rate capability 180 mAh g⁻¹ at a high rate of 20000 mA g⁻¹. This remarkable

electrochemical performance is due to the solution of the above mentioned problems of FeSe anode materials. For instance, the ultrafine FeSe NPs can short transport path of ions efficiently. The 3D carbon nanofiber aerogel can significant increase the conductivity, facilitate the diffusion of ions, and reduce the pulverization during the charge/discharge processes. Density functional theory (DFT) calculations reveal that a small energy barrier and negative adsorption energy of FeSe/carbon layer interface may result in fast Na ionic conductivity and more stable adsorption. The strong charge separation between FeSe NPs and carbon layer not only facilitates the intercalation of sodium into the FeSe NPs structure but also enhances the interfacial sodium storage.

2. Experimental and DFT calculations

2.1 Materials

Sodium alginate was purchased from the Bright Moon Seaweed Group (Qingdao, China). ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), selenium powder were purchased from Sinopharm Chemical Reagent (Shanghai, China), and used without further purification. Hydrochloric acid was purchased from the Shuangshuang Chemistry Company (Yantai, China). Deionized (DI) water (18 M Ω) was used in the synthesis.

2.2 Preparation of FeSe-CNFA-T and CNFA

An alginate solution (1 wt %) was poured into a $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution (2.5 wt %) under stirring (forming Fe cross-linked gelation), followed by the separation of gelation from the solution after 30 min and further washing clearly with distilled water. The as-prepared gelation was dehydrated via a freeze-drying process to obtain 3D Fe-alginate aerogels. The Fe-alginate aerogels were pyrolyzed at T °C ($T = 600, 700, 800$) with the heating rate of 2 °C min⁻¹ for 2 h in Ar atmosphere and then cooled down to room temperature naturally to obtain FeSe/CNFA- T . The resulting product was

collected, dried and mixed with selenium powder. The mixture was annealed at 600 °C for 2 h to obtain the desired FeSe-CNFA-T. Specifically, the FeSe/CNFA-700 was soaked into a 2 M hydrochloric acid solution for 10 h to remove the metal to obtain the CNFA.

2.3 Characterization

XRD patterns were characterized with X-ray diffractometer (DX2700, China) operating at Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray photoelectron spectroscopy (XPS) measurements were using an ESCALab250 electron spectrometer (Thermo Scientific Corporation) with monochromatic 150 W Al K α radiation. The morphology and structure of the samples were investigated by field-emission scanning electron microscopy (FESEM; JSM-7001F, JEOL, Japan). Transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDS) and high-resolution TEM (HRTEM) were obtained using a FEI Tecnai F20 electron microscope with an accelerating voltage of 200 kV. Thermogravimetric analysis measurement was carried out on an EXSTAR TG/DTA 6300 instrument (Seiko Instruments, Japan) in air. Raman spectroscopy were obtained on a Renishaw 1000 Raman spectrometer with the 514.5 nm excitation line of an Ar ion laser. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method from the data in a relative pressure (P/P_0) range between 0.05 and 0.20. The pore size distribution plots were derived from the adsorption branch of the isotherms based on the BJH model.

2.4 Electrochemical Measurements

The electrochemical characterizations of the prepared were carried out using the CR2025 coin type cells with sodium metal as the counter electrode at room temperature.

The electrolyte was 1.0 M NaCF_3SO_3 in DIGLYME (100 Vol %). The working electrode was mixed by compressing a mixture of the active materials, conductive carbon black, and binder (polyvinylidene fluorid, PVDF) in a weight ratio of FeSe-CNFA-T : carbon black : PVDF = 8:1:1 to form the slurry. The slurry was uniformly pasted onto a copper foil current collector. The cells were assembled in an argon-filled glove box with the concentrations of moisture and oxygen at below 1 ppm. Cyclic voltammetry tests were carried out using CHI 760E electrochemical workstation. The electrode capacity was measured by a galvanostatic charge/discharge method at a battery test system (Land CT2001A). The specific capacity of the samples is based on the total mass of the whole electrode.

2.4 DFT calculations

First-principles calculations were performed by density functional theory (DFT) as implemented in Vennia ab initio simulation package (VASP) (version 5.3.2). The general gradient approximation (GGA) of Perdew and Wang (PW91) was used for the exchange–correlation functional. The projector augmented wave (PAW) method was put into use to describe the interactions between valence electrons and the ionic cores. The energy cutoff was set as 450 eV and $3 \times 3 \times 1$ k-point mesh was used for Brillouin zone. The energy convergence standard was selected to be 10^{-5} eV and the force convergence standard to be $0.01 \text{ eV } \text{\AA}^{-1}$. Besides van der Waals interactions were accounted for using the DFT-D₃ method of Grimme.

3. Results and discussion

3.1 Characterization of FeSe-CNFA-T.

A three-step seaweed-derived strategy was developed to prepare FeSe NPs/carbon nanofiber aerogels (FeSe-CNFA) (**Fig. 1**). Firstly, the Fe-alginate

aerogels with macroporous architectures were synthesized *via* freeze-drying method using sodium alginate (SA) and FeCl_3 as precursors. The special “egg-

Fig. 1 Schematic illustration on the synthesis process of FeSe-CNFA.

box” structure in SA after ion-exchange with Fe^{3+} cations guides the initial formation of Fe-alginate hydrogels [28]. During the quick freezing process, dendritic ice crystals grew along the thermal gradient through the Fe-alginate hydrogels, and the Fe-alginate hydrogels sheets were concentrated between these ice crystals. After subliming the ice crystals, Fe-alginate hydrogels converted to Fe-alginate aerogels with 3D pore structure. Secondly, the obtained samples were pyrolyzed at T °C ($T = 600, 700$ and 800) in argon gas to obtain 3D net-like carbon nanofiber aerogel with embedded Fe NPs in single carbon nanofiber (Fe-CNFA-T). The diffraction peaks of body-centered cubic Fe NPs appear in the powder X-ray diffraction (PXRD) pattern of Fe-CNFA-T (**Fig. S1**). In this carbonization process, the confined Fe ions in “egg box” were reduced into Fe NPs with the pyrolysis of alginate macromolecules. These Fe NPs then catalyzed the alginate macromolecules into a 3D carbon nanofiber aerogel (**Fig. S2**) [29]. Finally, the embedded Fe NPs in the carbon nanofibers converted to FeSe NPs by annealing Fe-CNFA-T samples at 600 °C with Se powder for 2 h.

PXRD was used to record the structure evolution from Fe-alginate aerogel to FeSe-CNFA-T (**Fig. 2a**). FeSe-CNFA-T display four diffraction peaks at $2\theta = 32.5^\circ, 42.3^\circ, 50.8^\circ$, and 61.6° , corresponding to (101), (102), (110), and (103)

Fig. 2 (a) XRD patterns of FeSe-CNFA-T. The high resolution XPS spectra of FeSe-CNFA-700 (b), (c) Se 3d and (d) Fe 2p.

planes of tetragonal layered FeSe (JCPDS 73-8671). As displayed in **Fig. S3**, the tetragonal FeSe has a typical layered structure, where one unit cell consists of three atomic layers (one Fe layer and two Se layers) along the (001) crystal direction. The PXRD patterns of FeSe-CNFA-T show that the characteristic peaks of FeSe become sharper as the increase of temperature, indicating increased NP size of FeSe [30]. The X-ray photoelectron spectroscopy (XPS) survey spectrum in **Fig. 2b** of FeSe-CNFA-700 confirms the presence of Fe, Se, O and C signals. The C1s peaks shown in **Fig. S4** can be attributed to sp^2 -bonded

Fig. 3 SEM images of (a, b) FeSe-CNFA-600, (d, e) FeSe-CNFA-700, and (g, h) FeSe-CNFA-800. EDS mapping of (c) FeSe-CNFA-600, (f) FeSe-CNFA-700, and (i) FeSe-CNFA-800.

carbon (C–C), epoxy and alkoxy groups (C–O), and carbonyl and carboxylic (C=O) groups, which correspond to peaks at 284.6, 285.7, and 288.6 eV, respectively. The sharp XPS peak at 284.6 eV indicates the thermal reduction of macromolecule into carbon during the preparation process of Fe-CNFA [21]. The Se 3d shows two main peaks located at 55.6 eV (Se 3d_{5/2}) and 56.4 eV (Se 3d_{3/2}), which are also consistent with iron selenides (**Fig. 2c**) [31]. In the Fe 2p spectrum (**Fig. 2d**), the main peaks appear at the binding energies of 710.7 eV for Fe 2p_{3/2} and 724.7 eV for Fe 2p_{1/2} [24]. XPS chemical percentages between Fe: Se was

47:53. The extra small amount of selenium is due to selenium residue on carbon materials during selenide process.

The morphology and structure of the prepared FeSe-CNFA-T hybrids were investigated by using field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM). **Fig. 3a** shows the FESEM images of FeSe-CNFA-600, where few carbon nanofibers are observed from the carbon aerogel. When the pyrolysis temperature rose to 700 °C, a 3D net-like carbon nanofiber aerogel was formed in FeSe-CNFA-700 (**Fig. 3b**). The FeSe NPs are very small and are embedded by the carbon nanofibers. However, as shown in **Fig. 3c**, the FeSe NPs aggregate into large particles (~100-200 nm) and remain outside the carbon nanofiber matrix (FeSe-CNFA-800) caused temperature rising. **Fig. 3d** exhibits the EDS element mappings of FeSe-CNFA-700, showing the distribution of C, Fe, and Se. Fe and Se intensively distribute in NPs and C uniformly distributes in the whole material. The carbon nanofiber aerogel matrix displays high specific surface area and typical hierarchical micro/meso/macroporous structure.

The TEM and HRTEM images of FeSe-CNFA-700 are displayed in **Fig.3**. It can be seen that the ultrafine FeSe NPs are uniformly distributed on the surface or embedded into the carbon nanofibers (**Fig. 4a and 3b**). The HRTEM image of FeSe-CNFA-700 in **Fig. 4c** shows that FeSe NPs with diameter of ~ 5 nm are uniformly distributed in a single carbon nanofiber. The magnified HRTEM image in **Fig. 4d** reveals clear lattice fringes separated by 0.277 nm, which corresponds to the (101) crystal plane of FeSe. The morphology of layered FeSe NPs on carbon nanofiber is schematically illustrated in **Fig. 4e**. The large interlayer

Fig. 4 (a, b) TEM and (c, d) HRTEM images of FeSe-CNFA-700. (e) Schematic illustration of FeSe nanoparticles within 3D carbon nanofiber aerogels and FeSe with carbon layer.

spacing of layered FeSe NPs will result in more sodium ion intercalations and buffer the large volume change during sodiation and desodiation processes. The carbon layer can facilitate the electron transfer and Na⁺ transportation, which is crucial for high rate charge/discharge. Furthermore, the strong interaction between FeSe NPs and carbon layer results in enhanced interfacial sodium storage at the FeSe/carbon layer interface, which plays a critical role on its

remarkable long-term cycle stability and will be further confirmed by DFT calculation. Compared with FeSe-CNFA-700, As shown in **Fig. S5 and S6**, small NPs appear at FeSe-CNFA-600 with poor crystallinity and large particles remain outside the carbon nanofiber matrix (FeSe-CNFA-800).

The Brunauer–Emmett–Teller (BET) specific surface area of the samples were estimated to be $181 \text{ m}^2 \text{ g}^{-1}$ (FeSe-CNFA-600), $262 \text{ m}^2 \text{ g}^{-1}$ (FeSe-CNFA-700) and $215 \text{ m}^2 \text{ g}^{-1}$ (FeSe-CNFA-800), respectively. As shown in **Fig. 5a and 5b**, the N_2 adsorption/desorption isotherms of the FeSe-CNFA-T show a combination of type-IV adsorption isotherm indicating the existence of micro- and mesopores in the carbon nanofiber. The pore size distributions of FeSe-CNFA-T calculated from the adsorption branch of the isotherms show that the FeSe-CNFA-T own micropores and small mesopores, which is attributed to the thermal decomposition of alginate macromolecule. These pores can lead to sufficient electrode/electrolyte interface and fast ion transport pathways to promote rapid charge transfer. Also, there exists abundant macropores formed during the freeze-drying process. The ion-buffering reservoirs can be formed in the macropores that can minimize the ions diffusion distances among the carbon nanofibers. Raman spectroscopy was conducted to evaluate the graphitization degree of carbon aerogel in FeSe-CNFA-T. As shown in **Fig. 5c**, two broad peaks are centered at ~ 1323 and $\sim 1598 \text{ cm}^{-1}$, which are attributed to the D and G bands of the graphitic carbon, respectively. The intensity ratios of D and G bands (I_D/I_G) were calculated to be 1.04 (FeSe-CNFA-600), 1.00 (FeSe-CNFA-700), 0.96 (FeSe-CNFA-800), respectively. The low intensity ratio of I_D/I_G (0.96) in Raman spectrum is due to the high graphitic quality of the aerogel support in FeSe-

Fig. 5 (a) Porosity characterization, (b) Pore size distribution and (c) Raman spectra of FeSe-CNFA-T.

CNFA-800. The carbon contents of the obtained FeSe-CNFA-T were studied by the thermogravimetric analysis (TGA) measurement. As exhibited in **Fig. S7**, the conversion reaction of FeSe into FeSeO_x resulted in a weight increase at 150 °C. The weight loss observed at around 350 °C was attributed to the decomposition of FeSe and FeSeO_x into Fe_2O_3 and the combustion of carbon nanofiber. The weight percentages of the carbon nanofibers were measured to be 30-40 wt %.

3.2 The electrochemical characterization of the FeSe-CNFA-T

The electrochemical performance of sodium storage in the FeSe-CNFA-T were investigated using the CR2025 type cells. **Fig. 6a, S8 and S9** show the first three cyclic voltammetry (CV) curves of the FeSe-CNFA-T anodes at a scan rate of 0.1 mV s^{-1} and in the potential window of 0.01–3.00 V vs. Na^+/Na . For the FeSe-CNFA-T nanocomposites, the first cathodic scan of FeSe-CNFA-T shows three distinct peaks located at ~ 1.15 , ~ 0.78 , and ~ 0.48 V, respectively. The sharp reduction peak located at ~ 1.15 V is attributed to the formation of Na_xFeSe and a solid electrolyte interphase (SEI) by electrolyte decomposition. During the anodic scans, the peaks located at 1.57 and 2.04 V are assigned to the conversion reactions from Se in Na_xFeSe and FeSe. The cathodic scans from the second

Fig. 6 (a) CV curves of FeSe-CNFA-700 electrode at a scan rate of 0.1 mV s⁻¹. (b) Galvanostatic charge-discharge curves of FeSe-CNFA-700 electrode at the 1st, 2nd, and 3th between 0.01 and 3.0 V (vs Na⁺/Na) at a current density of 100 mA g⁻¹. (c) Cycling performance of FeSe-CNFA-T electrode in the voltage window of 0.01–3.0 V at 200 mA g⁻¹. (d) Rate performances of FeSe-CNFA-T electrode. (e) Long-term cycle stability of FeSe-CNFA-700 at a high current density of 2000 mA g⁻¹ over 1000 cycles.

cycle onward show distinct reduction peaks at ~ 0.78 V. The subsequent charge/discharge CV curves tend to be stable, indicating the FeSe-CNFA-700 exhibits good stability toward sodiation/desodiation. The discharge and charge

curves of the FeSe-CNFA-T sample at a current density of 100 mA g^{-1} are shown in **Fig. 6b, S10 and S11**. The first discharge curve exhibited a plateau at $\sim 1.17 \text{ V}$, followed by a gradual sloping tail down to the cutoff voltage. In subsequent cycles, the original plateau immediately vanished, and instead, one individual short plateaus gradually emerged and established, located at approximately $\sim 0.75 \text{ V}$. Such a multistage discharge profile is in perfect agreement with that of CV curves. The initial discharge capacity of sample FeSe-CNFA-700 is 594 mAh g^{-1} , and the initial charge capacity is 409 mAh g^{-1} corresponding to the initial Coulomb efficiency of 68.8 % (**Fig. 6b**). The FeSe-CNFA-600 and FeSe-CNFA-800 electrode can deliver an initial discharge capacity of 511 and 572 mA h g^{-1} (**Fig. S10 and S11**). These values are lower than that of FeSe-CNFA-700. In addition, the second discharge capacities of all the samples reduce slightly (the irreversible capacity loss) due to the formation of the SEI.

The cycling performance at 200 mA g^{-1} of FeSe-CNFA-600, FeSe-CNFA-700 and FeSe-CNFA-800 are compared in **Fig. 6c**. FeSe-CNFA-700 shows the high charge capacity of 380 mAh g^{-1} after 150 cycles with a capacity retention of 97 % at 200 mA g^{-1} , which is higher than those of FeSe-CNFA-800 (340 mAh g^{-1}) and FeSe-CNFA-600 (290 mAh g^{-1}). Additionally, the rate performance of these samples is displayed in **Fig. 6d**, which show a trend similar to the one in **Fig. 6d**. The average charge capacity of FeSe-CNFA-700 is 409, 370, 348, 361, 326 and 291 mAh g^{-1} at current densities of 100, 200, 500, 1000, 2000, and 5000 mA g^{-1} , respectively. Even at an extremely high rate of 20000 mA g^{-1} , the overall reversible capacity is still retained at 180 mAh g^{-1} . We also investigated the cycling performance of FeSe-CNFA-700. As shown in **Fig. 6e**, its discharge

Fig. 7 (a) CV curves at different scan rates and (b) corresponding log (i) versus log (v) plots at each redox peak (peak current: i, scan rate: v of the as-prepared FeSe-CNFA-700. (c) bar chart showing the percent of pseudocapacitive contribution at different scan rates. (d) CV curve with the pseudocapacitive fraction shown by the darkly cyan region at a scan rate of 1 mV s⁻¹. (e) EIS curves and the corresponding equivalent circuit (inset of (j)) of the coin cell. (f) The linear fits of the Z'' versus $\omega^{-1/2}$ in the low-frequency region.

specific capacity still maintains 313 mAh g⁻¹ after 1000 cycles at 2000 mA g⁻¹. CNFA. The performance of the CNFA in terms of specific capacity and cycling

stability was compared with that of FeSe-CNFA-*T*. As shown in Fig. S12 CNFA exhibits excellent cycling performance but low reversible capacity (50 mAh g^{-1} at 200 mA g^{-1} over 150 cycles), which suggests that such pure carbon material is not a high performance anode material compared with FeSe-CNFA-*T* for SIBs. The sodium storage properties of FeSe-CNFA-700 in terms of cycling stability and rate capability are among the best FeSe anode materials reported so far, suggesting the effectiveness of our electrode design in improving the electrochemical performance. We also investigated the current response behavior of FeSe-CNFA-700 at scan rates of $0.1\text{-}2.5 \text{ mV s}^{-1}$ (**Fig. 7a**). It is possible to mathematically analyze the transition in the time dependence of peak current, i.e., the peak reaction rate, which is a well-known approach to determine the onset of diffusional limitations [32-36]. A *b*-value of 0.5 is a straight forward outcome of Fick's law and signals a diffusion-limited process. A *b*-value of 1 is a standard expression for any activation (i.e., interface) polarization reaction. As shown in **Fig. 7b**, it exhibits a series of *b* values of 0.72 (peak 1) and 0.76 (peak 2). This represents a high capacitive contribution for the FeSe-CNFA-700 electrode. It leads to a fast Na^+ intercalation/extraction and durable cyclic stability. The pseudocapacitive contribution is calculated by Equation: $i = k_1v + k_2v^{1/2}$, in which k_1v and $k_2v^{1/2}$ represent the pseudocapacitive and inserted contributions, respectively. The pseudocapacitive contributions are 59, 64, 69, 76, 82, 86, 89 and 92 % at scan rates of 0.1, 0.3, 0.5, 0.7, 1.0, 1.5, 2.0 and 2.5 mV s^{-1} , respectively (**Fig. 7c**). With the increase of the sweep rates, the contribution of pseudocapacitive charge-storage increases obviously. It provides evidence that the higher ratio of the pseudocapacitive contribution enables faster Na^+ transport.

For example, at a sweep rate of 1 mV s^{-1} , around 76% of the stored charge is attributed to the capacitive process as indicated by the shadow area shown in the inset of **Fig. 7d**, especially at potentials deviating from the sodium insertion/deinsertion peaks [37-38].

Electrochemical impedance spectroscopy (EIS) was further used to calculate the D_{Na^+} quantitatively. The **Fig. 7e** is the equivalent circuit model of the EIS curves. The diffusion coefficient of the Na ions (D_{Na^+}) can be estimated from the low frequency region of the Nyquist plots according to the following equation.

$$D_{\text{Na}^+} = 0.5R^2T^3/A^2n^4F^4C^2\sigma^2$$

In the equation, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T represents the absolute temperature (298 K), A is the active surface area of the electrode/electrolyte interface (0.785 cm^2), n is the number of the transferred electrons ($n = 1$), F is the Faraday constant (96500 C mol^{-1}), C is the bulk concentration (which was $\approx 0.8 \times 10^{-3} \text{ mol cm}^{-3}$), and σ is the Warburg coefficient, which is determined as the slope of Z' versus $\omega^{-1/2}$ in the low frequency region ($\sigma = dZ'/d\omega^{-1/2}$). The linear relationship between Z' and $\omega^{-1/2}$ is shown in **Fig. 7f**. The slope σ of FeSe-CNFA-700 is calculated to be $690 \Omega \text{ s}^{-1/2}$. Therefore, the value of D_{Na^+} of the electrode is calculated to be $2.3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, similar to those of FeSe-CNFA-600 ($1.8 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$), and FeSe-CNFA-800 ($1.1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) anodes. This result indicates that the 3D carbon nanofiber aerogels are favorable for improving the Na ion diffusion processes, since the Na ions can diffuse promptly along the 1D carbon nanofiber.

3.3 The DFT calculation of the FeSe-CNFA-700

To understand this effect on the enhanced sodium storage performance of FeSe-CNFA-T hybrids, we performed DFT calculations to investigate the Na

Fig. 8 Models of (a) the graphene, (b) FeSe (001) surface, and (c) FeSe/carbon layer interface. Red, Na; cyan, Fe; gray, C; yellow, Se. (d) Minimum energy paths for sodium in FeSe (001) surface and FeSe/carbon layer interface. Diffusion paths of Na in (e) FeSe (001) surface and (f) FeSe/carbon layer interface. Side views of the models with an increase of Na coverage from 1 to 9 on (g) the FeSe (001) surface and (h) at the FeSe/carbon layer interface. (i) Binding energies per Na atom with an increase of Na coverage on the FeSe (001) surface and at the FeSe/carbon layer interface, respectively. (j) The charge-density difference at the interface.

adsorption process on the FeSe (001) surface and at the FeSe/carbon layer interface at atomic levels [16-17, 39-43]. **Fig. 8a-c** shows the models of carbon

layer, FeSe (001) phase, and FeSe/carbon layer interface, respectively. The carbon layer was modelled by 70 carbon atoms. The FeSe (001) surface was modelled by p (4 × 5) periodic slab supercell with two FeSe layers. One carbon layer was epitaxially placed above the surface to model the FeSe/carbon layer interface. The influence of carbon layer on the Na diffusion barrier from one site to the nearest site was considered, as shown in **Fig. 8d and S13**. It can be seen that FeSe/carbon layer interface has the lowest activation barrier (0.14 eV), followed by FeSe (001) surface (0.34 eV) and carbon layer (0.42 eV). The minimum energy paths of intercalated Na ions along *a* axis are shown in **Fig. 8e, 8f and S14**. The small energy barrier of FeSe/carbon layer interface may give rise to fast Na ionic conductivity. **Fig. 8g and 8h** show side views of the most stable models for the FeSe (001) facet and FeSe/carbon layer interface with an increase of Na coverage from 1 to 9. The adsorption energy is defined as $E_b = (E_{\text{Na/surf}} - E_{\text{surf}})/n - E_{\text{Na}}$, where $E_{\text{Na/surf}}$ and E_{surf} are the total energies of the surface with and without *n* Na atoms adsorbed, respectively, and E_{Na} is the energy of one Na atom in the bulk position. A more negative E_b indicates a more stable adsorption. As shown in **Fig. 8i**, the binding energy decreases with an increase of Na coverage, and in general the FeSe/carbon layer interface is able to provide higher binding energies than the bare FeSe surface. For one Na atom where the most stable adsorption site is between two Se atoms on the surface, the binding energies are 0.30 on carbon layer, −1.82 eV on FeSe and −1.95 eV at the FeSe/carbon layer interface, respectively. For one monolayer coverage, the binding energy per Na atom decreases to −0.18 eV on FeSe and −0.31 eV at the FeSe/carbon layer interface. The values of binding energies get close to 0 eV, indicating that it is

approaching the maximum Na accommodation. Moreover, the carbon layer can act as a second electron acceptor for accepting the negative charges that originally are stored in Na atoms. We can see that the addition of carbon layer results in the rearrangement of the electron density around Na atom, namely, the charge configuration of Na atom is transferred from the periphery of Fe and Se atom to the periphery of carbon layer in **Fig. 8j**. These results clearly prove the charge separation at the interface of FeSe/carbon layer interface, which results in a more favorable Na adsorption during sodiation/desodiation and thus enhanced sodium storage performance.

4. Conclusions

In summary, we report an sustainable seaweed-based approach to prepare ultrafine FeSe NPs (~ 5 nm) embedding in 3D network carbon nanofiber aerogel. The products are composed of FeSe NPs and interconnected carbon nanofiber networks with large surface area. As a potential anode material for SIBs, the FeSe-CNFA-700 demonstrates exceptional long-term cycle stability up to 1000 cycles (313 mA h g^{-1} at 2000 mA g^{-1}) and ultrahigh rate capability up to 20000 mA g^{-1} . Through in-depth analysis of the sodium storage behavior, the dominating pseudocapacitive charge storage and fast Na ion diffusion processes are thought to be the major factors contributing to the remarkable electrochemical performance. The results confirm the intercalation of Na^+ ions into the 3D ultrafine FeSe NPs/carbon nanofiber aerogel is enhanced through the strong interaction between FeSe NPs and the carbon layer. Furthermore, DFT calculations reveal that the unique FeSe/carbon layer interface in 3D network structure can enhance Na ion storage due to the small energy barrier and negative adsorption energy.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at doi.

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